

Preparation, evaluation and characterization of copper catalysts for ethanol fuelled diesel engines

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Abstract

Copper-based monolithic honeycomb catalysts for ethanol fuelled diesel engines have been prepared and evaluated. The washcoat consisted either of alumina or titania. Two different methods to apply the active material were used; incipient wetness impregnation and deposition precipitation. The catalysts have been evaluated in a laboratory reactor and have been characterised using SEM, XRPD, TEM, TPR, XPS, BET surface area and pore-size distribution measurements. Both the choice of washcoat material as well as the preparation method is of importance. Titania as washcoat gave a better performing catalyst than alumina in this case. Deposition precipitation gave a better catalyst than incipient wetness impregnation when alumina was used as washcoat, as well as at low temperatures for titania catalysts. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

This paper presents part of a study whose aim is to develop exhaust gas catalysts for ethanol fuelled diesel engines running in inner city traffic. Previous studies [1] have shown that even though precious-metal based catalysts are more active when it comes to converting both ethanol and carbon monoxide present in the exhaust, the selectivity towards complete combustion is higher over copper based catalysts. This is why two parallel studies have been performed, one with copper as the active material, which is presented here, and one with precious metals as active material [2].

It is well known that the preparation procedure may strongly affect the properties of the final catalyst. Two different preparation methods have therefore, been compared in this particular application, one where the active material was applied to the already washcoated monolith by incipient wetness impregnation, and one where the active material was precipitated onto the washcoat material prior to the washcoating of the monolith. Alumina and titania have been compared as washcoat materials.

Ethanol oxidation catalysts for the same application have been studied by, among others, McCabe and Mitchell [3,4], who have published a series of papers concerning catalysts for both ethanol and methanol fuelled vehicles. The performance of both noble metals and base metal oxides as catalytically active material for ethanol and acetaldehyde oxidation have been

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examined, supported on various materials. They found that platinum was not only more active than base metal oxides, but it also produced less of the unwanted by-product acetaldehyde. This is partly contradictory to our own experiences, where copper oxide catalysts were more selective than precious metal catalysts [1], probably due to the numerous differences in experimental conditions between the studies. A commercial hopcalite catalyst (CuO-MnO_2) was found to be as active and selective as the tested platinum catalyst, but it was irreversibly deactivated.

A large number of catalysts with different active materials, both precious metals and base metal oxides, supported on alumina and zirconia, have been tested by Yu Yao [5]. Pt and Pd were found to be superior to all other catalysts in the study, both in activity and in selectivity towards complete oxidation of ethanol. Yu Yao also found that base metals supported on $\gamma\text{-Al}_2\text{O}_3$ were more active than when they were supported on ZrO_2 . Amongst the base metal oxide catalysts, $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ was the most active and was therefore, more thoroughly investigated concerning effects of metal loading and thermal ageing.

Gonzalez and Nagai [6] were inspired by the work of McCabe and Mitchell to further study the mechanisms in oxidation of ethanol. They used catalysts consisting of silica supported noble metals, such as Pt, Ru, Pt–Ru, Rh and Pd. Pt was most active, followed by Pt–Ru, but with a significant formation of acetic acid as a by-product at high temperatures. In a second paper [7] they presented the results from a study of the mechanisms of oxidation of both ethanol and acetaldehyde over Pt/SiO_2 prepared by both impregnation and ion exchange. The effect of using different pretreatment conditions was also examined.

Rajesh and Ozkan [8] have studied oxidation of ethanol over catalysts consisting of oxides of copper, oxides of chromium and combinations thereof, supported on γ -alumina pellets. They found that the Cu-containing catalysts were more selective towards complete oxidation of ethanol than the Cr-containing catalysts. 50% conversion was reached at a lower temperature over the Cr catalyst than over the Cu catalyst, while the opposite was true for 90% conversion.

Marques da Silva et al. [9] have investigated ethanol oxidation over $\text{Pt/Al}_2\text{O}_3$ catalysts, modified with rhodium and/or lanthanum oxide. They suggest that the reason for the decrease in acetaldehyde produc-

tion over bimetallic Pt–Rh catalysts when lanthanum oxide had been added to the alumina could be that the formation of Pt–Rh alloy thereby was prevented.

Barresi and Baldi [10] have studied the oxidation of ethanol in air over a monolithic platinum based commercial catalyst, and they proposed a reaction mechanism. They varied the inlet concentration of ethanol between 50 and 2000 ppm, and the space velocity between 70 000 and 200 000 h^{-1} , and found that this influenced both the total oxidation to carbon dioxide as well as the partial oxidation to acetaldehyde. With lean ethanol–air mixtures less acetaldehyde was formed.

Ismagilov et al. [11] have presented a study of oxidation of ethanol over unsupported CuO , $\text{CuO/Al}_2\text{O}_3$ and $\text{Pt/Al}_2\text{O}_3$. They have determined the reaction orders and the activation energies for both partial and complete oxidation, and investigated the effect of adding water vapour to the reaction gas mixture. In a later paper [12] they suggested a reaction mechanism for oxidation of ethanol to acetaldehyde over $\text{CuO/Al}_2\text{O}_3$.

Copper catalysts for ethanol oxidation in stationary applications have been studied by Larsson and Andersson [13]. They used catalysts consisting of copper oxide supported on titania and ceria-modified titania. The ceria did not only enhance the activity of the copper species, but also stabilised the surface area of the titania support.

However, most of the studies have been carried out in gas flows containing only a couple of gas components. We have tried to make the test gas composition as realistic as possible, compared with the exhaust gas from a real ethanol fuelled engine. We are also using monolithic catalysts, while most of the other studies have been carried out on pellet or powder catalysts.

2. Experimental

2.1. Catalyst preparation

The catalysts consisted of a monolithic honeycomb cordierite substrate (Corning, EX-20), a washcoat material of either γ -alumina or titania (anatase), and an active copper containing phase. Two different preparation methods have been applied; incipient wetness impregnation and deposition precipitation. According

to the literature [14,15] deposition precipitation should give a more homogeneous distribution of the active material onto the washcoat than impregnation. The catalyst samples had an external volume of approximately 13 cm³. The honeycomb substrate had a cell density of 62 cells/cm² (400 cells/in.²). The alumina used was from Condea (Puralox NGa-150, 145 m²/g) and the titania was from Rhône-Poulenc (Rhoditan DT51 D, 75–95 m²/g). The amount of washcoat on the catalysts was 150 g washcoat per dm³ of catalyst, that is approximately 1.95 g/sample. The calculated copper loading on each catalyst was 8 wt.% of the washcoat. The precursor was Cu(NO₃)₂·6H₂O (p.a., MERCK).

2.1.1. Incipient wetness impregnation

The cordierite substrate was dipped in an acidic slurry of 25 wt.% alumina or titania with 1 wt.% Bindzil[®] (Silica sol, 40/130, Eka Nobel) as a binder and 0.5 M HNO₃. The slurry had been stirred for 2 h at 800 rpm and ballmilled for 22 h. Each monolith was dipped 4–6 times. After each dip excess slurry was carefully removed by blowing air through the channels, the catalyst was dried at 200°C for 2 h, and was then weighed. When the right amount of washcoat had been applied, the catalyst was calcined in air for 2 h at 500°C.

The active material was applied by incipient wetness impregnation. The washcoated monolith was impregnated with an aqueous solution of copper nitrate. 2 ml of solution was used for each catalyst sample. The catalysts were dried in air in a slow ramp (ca. 2°C/min) from room temperature to 200°C, this temperature was maintained for 2 h, and was then increased (ca. 5°C/min) to the calcination temperature 500°C, where it was kept for 2 h.

2.1.2. Deposition precipitation

The procedure of the deposition precipitation was based on a method described by Carnö et al. [16]. An aqueous slurry of alumina or titania was mixed with an aqueous solution of copper nitrate and urea (MERCK). The copper/urea molar ratio was 1/9. The resulting slurry was stirred for 2 h and was ball milled for 22 h. It was heated in an oil bath to 90°C, where it was kept for 5 h under continuous stirring, and with nitrogen gas above the slurry to create an oxygen free atmosphere. The urea decomposed and the pH increased, causing

copper hydroxide ions to precipitate and anchor to the washcoat surface. After cooling, the substance was dried overnight at 200°C. The dry powder was then crushed, and a slurry was prepared by adding water and Bindzil[®]. The slurry was stirred for 2 h and ball milled for 22 h. A monolith was repeatedly dipped and dried as described in Section 2.1.1, until 1.95 g of alumina or titania, excluding the weight of the copper hydroxide, had been applied. The catalyst was calcined in air at 500°C for 2 h.

2.2. Catalyst evaluation

The performances of the catalysts were studied in a tubular reactor made of sintered alumina (inner diameter 25 mm). The reactor was placed in a furnace (ENTECH, 1.8 kW). The composition of the test gas (see Table 1) was chosen in order to simulate the exhaust from a diesel engine fuelled by ethanol, at 100% excess air ($\lambda = 2$). During the experiment, the temperature of the furnace was first increased from 70°C to 500°C, with approximately 5°C/min, and the temperature was kept at 500°C for 1 h. The test gas was thereafter changed to contain only nitrogen (80 vol%), oxygen (10 vol%) and steam (10 vol%) and the catalyst was allowed to cool to 70°C overnight. The second day the gas mixture was changed again to the test gas in Table 1 and the temperature was increased to 500°C with a heating rate of approximately 2°C/min. This final temperature ramp is the part of the experiment that is presented in Section 3, while the first part was used as a pretreatment.

The main part of the test-gas flow was mixed and preheated to 70°C before entering the reactor, but ethanol, carbon monoxide and nitric oxide were added close to the catalyst, in order to prevent the gases from reacting before they reached the catalyst.

Table 1
Test gas composition

Component	Concentration
O ₂	10 vol.%
H ₂ O	10 vol.%
CO ₂	6.5 vol.%
N ₂	73.4 vol.%
C ₂ H ₅ OH	200 ppm
NO	600 ppm
CO	300 ppm

Ethanol was evaporated by bubbling nitrogen through two consecutive ethanol containing glass cylinders with porous glass filters. A water bath kept the liquid ethanol (Kemetyl 99.5%) at room temperature. Dried and filtered air was supplied by the in-house system for compressed air and a constant flow of steam was provided by combustion of hydrogen in air over a Pt/Al₂O₃ catalyst (0.5 wt.% Pt, Johnson Matthey) in a steam generator. The rest of the gas components came from gas cylinders (AGA). Mass flow controllers monitored all gas flows. The space velocity was approximately 100 000 h⁻¹, overnight it was decreased to approximately 25 000 h⁻¹.

The concentration of total hydrocarbon in the resulting gas was measured continuously with a hydrocarbon analyser equipped with a flame ionization detector (JUM FID 3-300). NO, NO₂ and NO_x were analysed with a chemiluminescence analyser (ECO Physics CLD 700 EL-ht), CO with a non-dispersive infrared (NDIR) instrument from Maihak (UNOR 6N) and CO₂ and O₂ by NDIR and an electrochemical oxygen sensor, respectively, with a Rosemount NGA 2000 NDIR/EO₂ analyser. Detailed information of the concentrations of ethanol, acetaldehyde and other oxygenated hydrocarbons and hydrocarbons, was given in a semi-continuous way by an on-line gas chromatograph (GC) (Varian Star 3400 CX GC-3BT) equipped with two parallel columns (FFAP and GS-Q from J & W Scientific) and two flame ionization detectors. The GC was only used at the last part of the experiment, not during the pretreatment.

2.3. Characterization of catalyst material

After catalyst evaluation, each monolith was cut along the channel direction for visual analysis and representative samples were taken for further analysis. The morphology and element distribution in the washcoat materials were studied by use of a scanning electron microscope (SEM, JEOL JSM-880) equipped with an energy X-ray dispersive spectrometer (EDS, LINK ISIS, GEM). Catalyst coating, gently scratched from the catalyst, was studied by X-ray powder diffraction using a Guinier-Hägg camera, working with Cu K α radiation. Si was used as internal standard and the obtained photographs were evaluated in a computerised scanner system [17]. The records were

matched with tabulated JCPDS data. To study the morphology and element distribution on the nanometer scale a transmission electron microscope (JEOL 2000FX), equipped with an EDS-detector (LINK AN 10000), was used. The sample was transferred onto a hollow carbon film supported on a grid of nickel.

X-ray photoelectron spectroscopy (XPS) analyses were performed with a Kratos XSAM 800 instrument using a magnesium anode. Charging effects were corrected by adjusting the Al 2p peak to a position at 74.6 eV.

The temperature-programmed reduction (TPR) was performed in a Micromeritics AutoChem 2910. 50 cm³/min of a gas containing 10% H₂/Ar (AGA) passed through the quartz reactor containing a crushed part of the sample (total weight ca. 0.50 g). The temperature was increased by 10°C/min from ambient to 500°C. The water formed during the reduction was condensed in a cold-trap, containing a mixture of iso-propanol and liquid nitrogen, before the resulting gas passed a thermal conductivity detector, and the consumption of hydrogen was measured.

The BET surface area and the pore size distribution were determined in a Micromeritics ASAP 2000, using nitrogen as adsorptive.

3. Results and discussion

3.1. Catalyst evaluation

Fig. 1 shows the conversion of ethanol versus temperature for the four catalysts. The catalyst with alu-

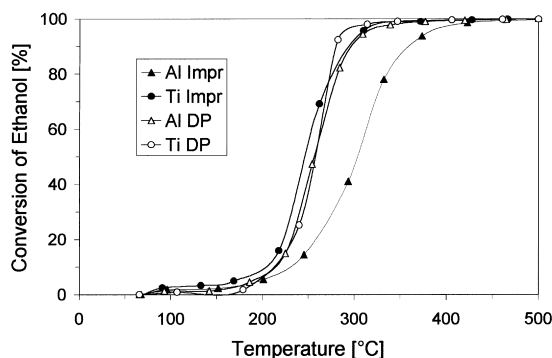


Fig. 1. Conversion of ethanol over copper catalysts with alumina (Al) or titania (Ti) washcoats, prepared by impregnation (Impr) or deposition precipitation (DP).

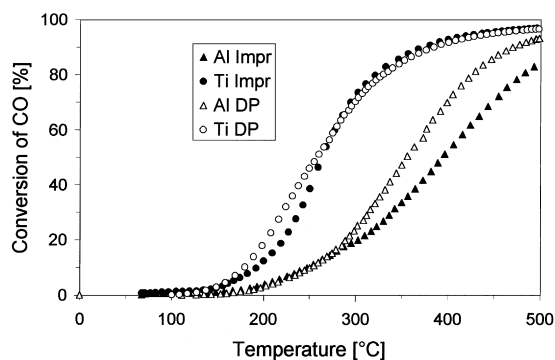


Fig. 2. Conversion of carbon monoxide over copper catalysts with alumina (Al) or titania (Ti) washcoats, prepared by impregnation (Impr) or deposition precipitation (DP).

mina washcoat, prepared by incipient wetness impregnation (Al-Impr), had a light-off temperature of 300°C (T_{50} , the temperature at which 50% of the ethanol is converted). The other three catalysts have similar behaviour, with light-off temperatures of approximately 250°C.

The picture is different when examining the conversion of carbon monoxide (see Fig. 2). Here the alumina based and the titania based catalysts are separated. The titania based catalysts showed better results than the alumina catalysts. Both titania catalysts had the same light-off temperature (250°C). The deposition precipitation prepared titania catalyst (Ti-DP) was slightly more active at temperatures below the light-off temperature, but above this temperature, Ti-DP and Ti-Impr behaved similarly. The catalyst Al-Impr still had the highest light-off temperature, 400°C, and it did not reach more than 80% conversion in this temperature interval. The light-off temperature for the deposition precipitation prepared alumina catalyst (Al-DP) was 350°C.

The reason why complete conversion was not reached is that some ethanol was converted to carbon monoxide, so CO was formed as well as converted at the same time, resulting in these curves. These results correspond to the results reported by other authors, who found that CO was formed by incomplete oxidation of ethanol at high temperatures [3,5], and that when both CO and ethanol were present in the inlet gas, the oxidation of CO was inhibited, since ethanol adsorbed stronger to the catalyst surface [5]. That was

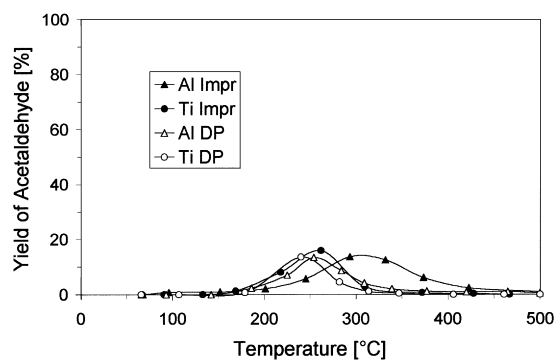


Fig. 3. Yield of acetaldehyde over copper catalysts with alumina (Al) or titania (Ti) washcoats, prepared by impregnation (Impr) or deposition precipitation (DP).

probably what we saw over the alumina supported catalysts, over which the oxidation of CO appeared at higher temperatures than the ethanol oxidation.

Another important aspect is the by-product formation, which must be as low as possible. The main by-product formed in this application is acetaldehyde, but small amounts of diethyl ether, methane and ethene have also been found. When precious metals have been used as active material, acetic acid has also been found as one of the by-products [1,2], but no acetic acid was detected in these experiments with copper based catalysts.

Fig. 3 shows the yield of acetaldehyde versus the temperature for the four catalysts. The yield is calculated as the amount of acetaldehyde formed divided by the amount of ethanol entering the reactor.

The maximum yield was about 15% for all the catalysts, but the peaks appear at different temperatures. Al-Impr produced acetaldehyde over the temperature interval between 200°C and 400°C, while the acetaldehyde production for the other three catalysts was limited to the interval between 200°C and 300°C.

Since nitrogen dioxide is more hazardous than nitric oxide, the concentration should be kept as low as possible at the street level, even though eventually all the NO is oxidised to NO₂ in the atmosphere. In Fig. 4 the formation of NO₂ is presented as the ratio between NO₂ and total NO_x in the resulting gas. More NO₂ was formed over the titania catalysts than over the alumina catalysts.

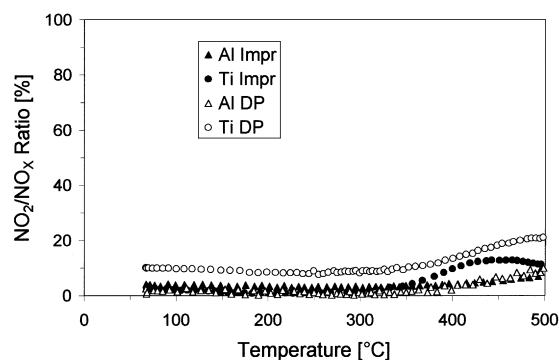


Fig. 4. Formation of nitrogen dioxide over copper catalysts with alumina (Al) or titania (Ti) washcoats, prepared by impregnation (Impr) or deposition precipitation (DP).

3.2. Catalyst characterization

3.2.1. Visual analysis

The impregnation prepared catalysts were not homogeneously coloured. Al-Impr was black on the outside, but the inside was mainly light green, with black zones at the inlet and outlet areas. Ti-Impr was also light green at the centre, and towards the ends of the monolith grey, brown and black zones were observed. The outside was black-grey. Black dots could be observed on the outer surfaces of both these catalysts.

The deposition precipitation prepared catalysts were more homogeneously coloured throughout the monolith. Al-DP had a grey-green colour, while Ti-DP was grey-brown. The washcoat of these catalysts was brittle and did not fasten as well as the washcoat of the catalysts prepared by the incipient wetness method.

3.2.2. Scanning electron microscopy (SEM)

Fig. 5 a–c show the element mapping of copper in the alumina washcoated catalysts. The copper is collected in large particles at the inlet and outlet of the channels of the incipient wetness impregnated sample (Fig. 5a), while it is more evenly spread at the centre of the catalyst (Fig. 5b). The back-scattered electron (BSE) images indicated that the surfaces at the inlet and outlet of Al-Impr were covered by particles of high copper content, which ranged from 200 to 1000 nm.

The deposition precipitation prepared sample, Al-DP, had well dispersed copper all over the catalyst

(Fig. 5c), with the exception of a few particles with high copper concentration. BSE images and copper maps of Ti-DP also indicated an even dispersion of copper on the sample.

The SEM-study showed that the catalysts that were prepared by deposition precipitation had more cracks in the washcoat than the incipient wetness prepared catalysts, which corresponds to the fact that the washcoats were relatively easily crumbled.

3.2.3. X-ray powder diffraction (XRPD)

For the impregnated alumina catalyst (Al-Impr) it was only in materials from the inlet and outlet of the monolith channels (the black material) that crystalline copper oxide (CuO) could be detected, and not in the middle. This, in combination with the element mapping of copper shown above, tells us that the copper oxide particles were larger at the edges than in the centre. The XRD pattern for deposition precipitation prepared Al-DP looked almost exactly the same as that for the centre of Al-Impr, with no peaks indicating copper oxide. The same result was achieved while comparing the titania catalysts, copper oxide could only be detected on the impregnated catalyst.

Other crystalline copper containing species than CuO were not detected in any of the catalysts.

3.2.4. Transmission electron microscopy (TEM)

An image of the material in the middle section of the impregnated alumina catalyst (Al-Impr) is shown in Fig. 6a. The image is dominated by stick-shaped particles corresponding to the morphology of the alumina. A number of EDS-measurements revealed that the green Al-Impr material consisted of about 5.0 at% Cu, and that copper was homogeneously distributed on or in the γ -Al₂O₃ material, since no particles with higher copper content could be observed on a nm-scale. In the deposition precipitation prepared sample similar morphology was observed, but spot measurements on a nm-scale showed significant variations in Cu/Al ratio. 30–80 nm particles with substantially higher Cu-content could also be observed in the material.

The average copper content in the examined areas was slightly higher in the Al-DP than in Al-Impr, possibly due to that the copper was collected in the large particles at the inlet and outlet of the latter sample.

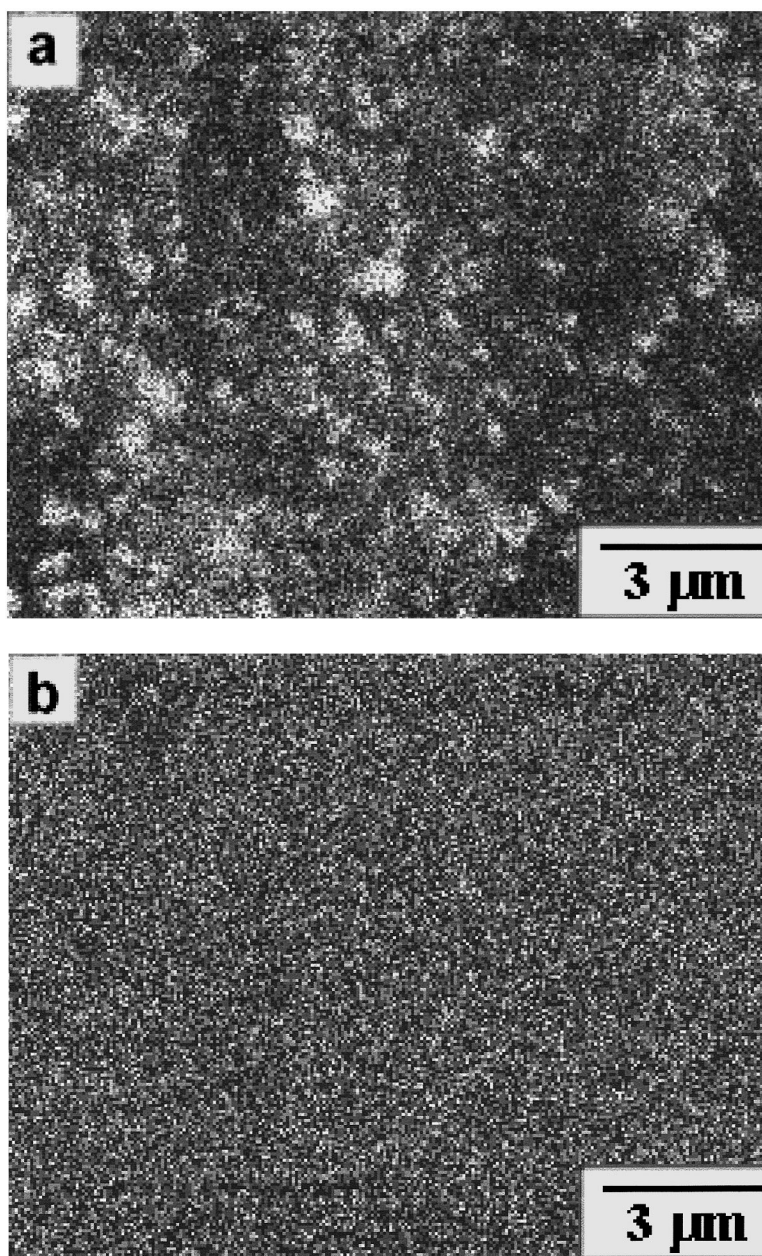


Fig. 5. Element mapping of copper (the presence is indicated by white spots) on (a) Al-Impr, at the outlet of the monolith, (b) Al-Impr, at the centre of the monolith and (c) Al-DP at the centre of the monolith.

Fig. 6b shows the material from the middle section of Ti-Impr. The morphology in this material is dominated by 20–30 nm crystals of TiO_2 . EDS measurements showed that the green material from Ti-Impr contained 6.0 at% Cu, homogeneously distributed in

the washcoat material. Careful comparison between the surfaces of calcined TiO_2 , without copper, and catalyst Ti-Impr showed that the latter was not as smooth as the former. These observations, and the fact that both materials yielded identical electron diffraction

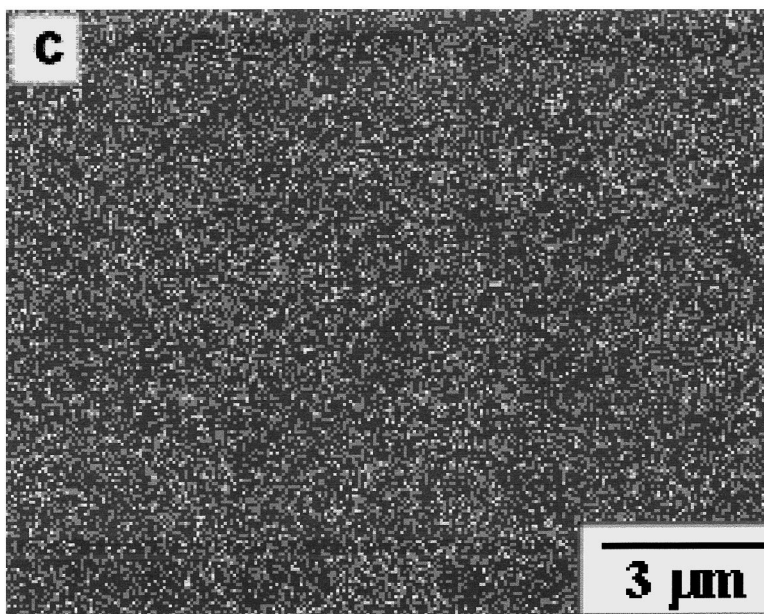


Fig. 5. (Continued).

(ED) patterns showing only anatase, might indicate that well dispersed copper compounds, e.g. CuO, was formed on the surface of the washcoat, and thereby roughened it.

Material from the grey zone on the monolith contained, beside the homogeneously covered material, 20–30 nm spherical crystals with high Cu-content, and in the material from the brown zone corresponding crystals of sizes 30–100 nm was observed. This shows, as in the Al-Impr catalyst, that the Cu content increased from the centre towards the inlets and outlets of the monoliths.

The grey-brown material from the middle of the Ti-DP consisted of titania, within which copper rich crystallites of 20–40 nm were found.

To summarise these results we can conclude that the distribution of Cu in the materials is reflected by the changes in colour, thus the light green material corresponds to copper well dispersed on the washcoat materials, whereas the grey, brown and black zones correspond to an increase in size and amount of CuO.

3.2.5. X-ray photoelectron spectroscopy (XPS)

Al-Impr and Al-DP were compared with XPS. Both samples had both Cu²⁺ and Cu⁺ present, Cu²⁺

was dominating. However, more Cu⁺ was found in Al-Impr than in Al-DP. Cu²⁺ at the inlet and outlet of Al-Impr could be identified as CuO, which corresponds to the results from XRPD. The amount of copper at the inlet and outlet of Al-Impr is considerably higher than in the middle of the same sample as well as in Al-DP. This could also be seen in the SEM and TEM analyses.

3.2.6. Temperature-programmed reduction (TPR)

In Fig. 7 the TPR profiles of all four catalysts are compared with the TPR profile of a reference sample of unsupported CuO (Micromeritics). All catalyst samples were reduced at a temperature lower than that corresponding to the reference bulk CuO.

In the profile from the reference sample of CuO two unresolved peaks can be seen. The alumina samples show only one peak. Al-DP was somewhat more easily reduced than Al-Impr. Their maximums are separated by 10°C. Three peaks can be distinguished in the profiles of the Ti-samples, most obvious in Ti-Impr, even though they are overlapping. The high temperature peak of both the titania catalysts appear at approximately the same temperature as the single peak of the alumina catalysts, but the reduction starts at a lower temperature.

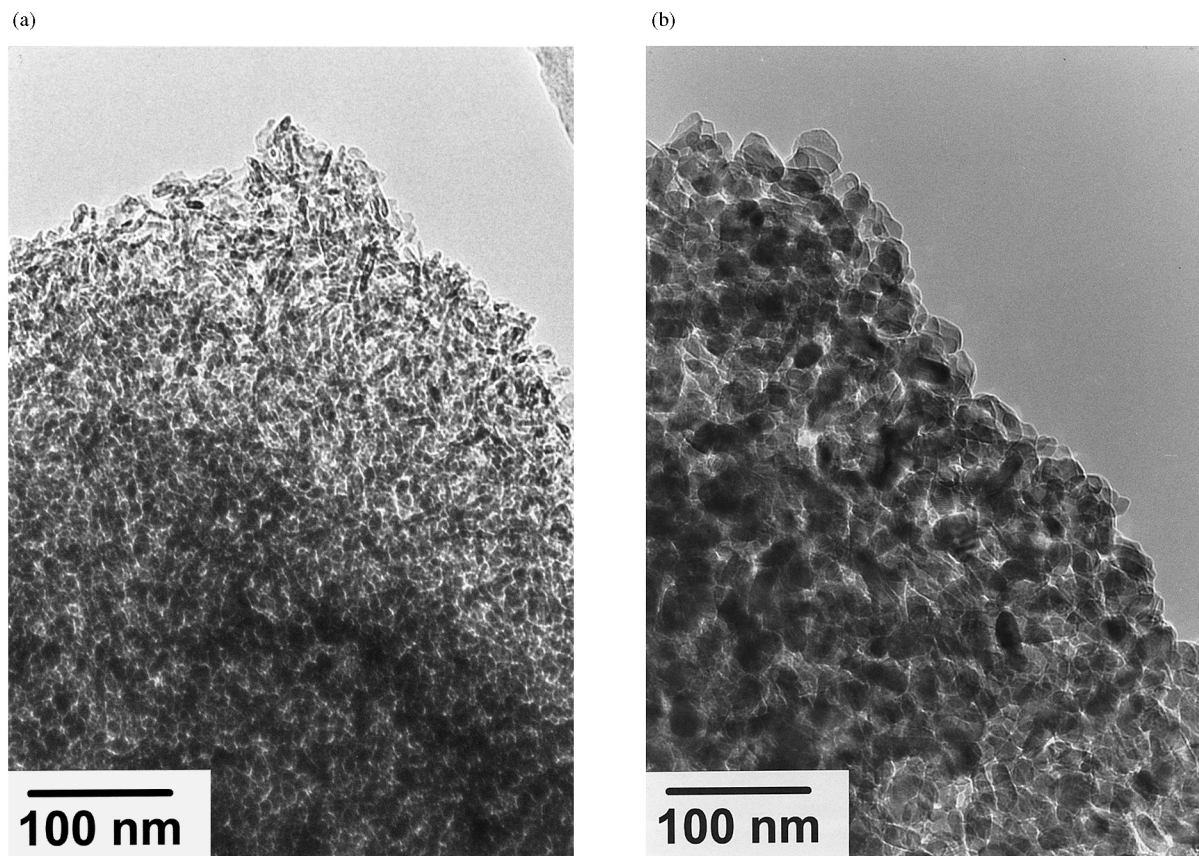


Fig. 6. TEM images of impregnated washcoat material from the middle section of (a) Al-Impr and (b) Ti-Impr.

After reduction all samples were grey-black, with the exception of the two impregnated samples, which also contained some red-brown parts.

No peaks were detected when the washcoat materials were analysed in this temperature range.

The reason why the supported copper species were more easily reduced than the reference sample could be a dispersion effect [18,19,20,21], but it could also be an effect of interaction between the support and the copper species [19,20].

The number of peaks can be explained in numerous ways. One suggestion why the reference CuO gave two peaks is that it was reduced in two steps, first from Cu^{2+} to Cu^+ and then to Cu^0 [20,22]. Multiple peaks could in the case of titania be an effect of stepwise reduction, as described above, or that some kind of Cu-Ti-compound has been formed, which is reduced at a different temperature than CuO [19,20].

Fig. 6. (Continued).

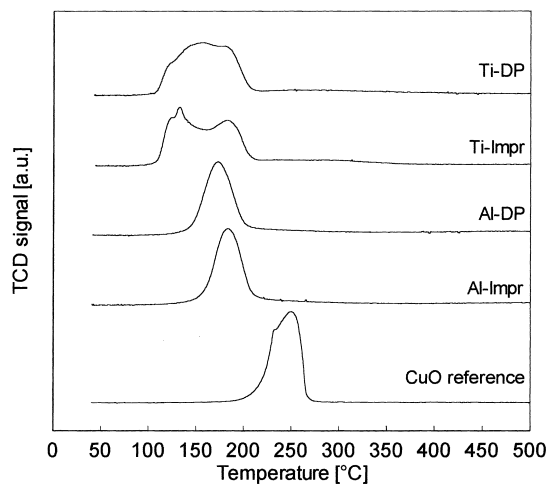


Fig. 7. TPR profiles for all four catalysts as well as unsupported reference CuO (Micromeritics).

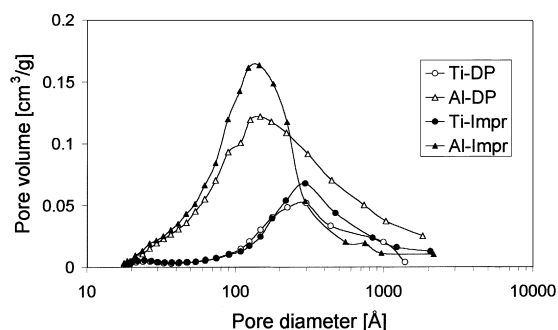


Fig. 8. Pore size distribution in the four catalysts tested, including the cordierite (BJH adsorption, $dV/d\log(D)$ pore volume).

It could also be an effect of various particle sizes, small particles being more easily reduced than larger ones [19,20,22], or pore size [23]. Neither of the two alumina-supported samples showed more than one single reduction peak. This could be an indication that the copper only exists in one form on the alumina, the particle size is very uniform, copper is only reduced in one step and that the alumina only acts as a dispersing agent for the copper species, without interacting with it. This is however, not very likely, since we have seen that the particle size varies at least in the impregnated sample, and that XPS has shown the presence also of Cu^+ , and formation of copper aluminate have been reported by others [19,24,25,26,27]. The lack of multiple peaks in this case could be that the species are reduced at the same temperatures so that the peaks are completely overlapping.

3.2.7. BET surface area and pore size distribution

The BET surface area of the alumina washcoat on the used catalysts was approximately $120\text{--}130\text{ m}^2/\text{g}$ after the evaluation, while the surface area of the titania was about five times as low. As the activities of the titania based catalysts were still higher than those of the corresponding alumina ones, we conclude that these higher activities could not be a washcoat surface area effect.

The alumina washcoats were more porous than the titania washcoats. Ti-Impr and Ti-DP had few pores smaller than 100 Å in diameter, while Al-Impr had few pores exceeding 300 Å (see Fig. 8).

The deposition precipitation prepared alumina catalyst had a broader pore size distribution than the corresponding impregnated catalyst. The larger pores

could originate from the gatherings of copper particles within the washcoat network seen in TEM, while the copper particles in the impregnated samples are spread over the washcoat surface, not giving rise to new pores. The pore size could explain why Al-Impr was the least active catalyst, if at the short residence time the gas did not diffuse into the small pores.

4. Conclusions

In ethanol oxidation, Al-Impr differed from the rest of the catalysts, having a light-off temperature well above the other catalysts tested. It also produced acetaldehyde over a broader temperature range compared to the others. Titania catalysts performed better than alumina catalysts in carbon monoxide oxidation, but they also produced more nitrogen dioxide.

The reason why the titania catalysts were more active could be that there is an interaction between the titania and the copper species dispersed over it, resulting in a higher activity. The surface area does not seem to be of a major importance in this case, since titania had much lower surface area than alumina. The least active catalyst, Al-Impr, had smaller pores than the rest of the catalysts. Diffusion into the small pores could be hindered at the rather high space velocity, hereby making less copper on this particular catalyst accessible to the gas.

The deposition precipitation prepared catalysts were more active than the corresponding incipient wetness impregnated catalysts. This was most obvious for the alumina catalysts, but could also be seen at low temperatures for titania catalysts. This could be explained by a more even distribution of the copper species over the surface. The copper content in the impregnated catalysts increased from the centre towards the inlets and outlets of the monolith channels, where CuO was identified. On the deposition precipitation prepared catalysts, and at the centre of the impregnated catalysts, the surface was covered by small well-dispersed copper containing particles. The large CuO particles in the impregnated samples was the only copper compound that has been identified, but it is likely that also other amorphous copper compounds were present on the catalysts, such as copper aluminate.

The distribution of Cu in the materials is reflected by the changes in colour, thus the light green material

correspond to copper well dispersed on the washcoat materials, and in the order grey, brown and black zones to an increase in size and amount of CuO.

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References

- [1] L.J. Pettersson, A.M. Wahlberg, S.G. Järås, *Stud. Surf. Sci. Catal.* 116 (1998) 465.
- [2] A. Wahlberg, L.J. Pettersson, E. Pelttersson, K-E. Egeback, J. Warren, Submitted for publication (1999).
- [3] R.W. McCabe, P.J. Mitchell, *Ind. Eng. Chem. Prod. Res. Dev.* 22 (1983) 212.
- [4] R.W. McCabe, P.J. Mitchell, *Ind. Eng. Chem. Prod. Res. Dev.* 23 (1984) 196.
- [5] Y.-F. Yu Yao, *Ind. Eng. Chem. Process Des. Dev.* 23 (1984) 60.
- [6] R.D. Gonzalez, M. Nagai, *Appl. Catal.* 18 (1985) 57.
- [7] M. Nagai, R.D. Gonzalez, *Ind. Eng. Chem. Prod. Res. Dev.* 24 (1985) 525.
- [8] H. Rajesh, U.S. Ozkan, *Ind. Eng. Chem. Res.* 32 (1993) 1622.
- [9] A. Marques da Silva, G. Corro, P. Marecot, J. Barbier, *Stud. Surf. Sci. Catal.* 116 (1998) 93.
- [10] A.A. Barresi, G. Baldi, *Chem. Eng. Commun.* 123 (1993) 17.
- [11] Z.R. Ismagilov, N.M. Dobrynkin, V.V. Popovskii, *React. Kinet. Catal. Lett.* 10(1) (1979) 55.
- [12] Z.R. Ismagilov, V.N. Bibin, V.V. Popovskii, N.M. Dobrynkin, *React. Kinet. Catal. Lett.* 23(1-2) (1983) 143.
- [13] P.-O. Larsson, A. Andersson, *J. Catal.* 179 (1998) 72.
- [14] J.W. Geus, in: G. Poncelet, P. Grange, P.A. Jacobs (Eds.), *Preparation of Catalysts III*, Elsevier, Amsterdam, 1983, p. 1.
- [15] X. Xiaoding, H. Vonk, A. Cybulski, J.A. Moulijn, *Stud. Surf. Sci. Catal.* 91 (1995) 1069.
- [16] J. Carnö, M. Ferrandon, E. Björnbohm, S. Järås, *Appl. Catal. A* 155 (1997) 265.
- [17] K.-E. Johansson, T. Palm, P.-E. Werner, *J. Phys. E3* (1980) 1289.
- [18] S.D. Robertson, B.D. McNicol, J.H. de Baas, S.C. Kloet, J.W. Jenkins, *J. Catal.* 37 (1975) 424.
- [19] S.J. Gentry, P.T. Walsh, *J. Chem. Soc., Faraday Trans. I* 78 (1982) 1515.
- [20] A. Wöllner, F. Lange, H. Knözinger, *Appl. Catal. A* 94 (1993) 181.
- [21] C.J.G. van der Grift, A. Mulder, J.W. Geus, *Appl. Catal.* 60 (1990) 181.
- [22] W.-P. Dow, T.-J. Huang, *Appl. Catal. A* 141 (1996) 17.
- [23] B. Mile, D. Stirling, M.A. Zammitt, A. Lovell, M. Webb, *J. Catal.* 114 (1988) 217.
- [24] A. Wolberg, J.F. Roth, *J. Catal.* 15 (1969) 250.
- [25] R.M. Friedman, J.J. Freeman, F.W. Lytle, *J. Catal.* 55 (1978) 10.
- [26] X.-Y. Jiang, R.-X. Zhou, P. Pan, B. Zhu, X.-X. Yuan, X.-M. Zheng, *Appl. Catal. A* 150 (1997) 131.
- [27] F. Severino, J.L. Brito, J. Laine, J.L.G. Fierro, A. López Agudo, *J. Catal.* 177 (1998) 82.